



Faculty of Resource Science and Technology

**Preparation and Characterization of Electrically Conductive Polymer-Polyethylene  
Terephthalate (PET) Film**

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**Preparation and Characterization of Electrically Conductive Polymer- Polyethylene  
Terephthalate (PET) Film**

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A project proposal submitted in partial fulfilment of the  
Final Year Project (STF 3013) Course

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## **Declaration**

I hereby declare that no portion of the work referred to in this dissertation has been submitted in support of an application for another degree or qualification to this university or any other institution of higher learning.

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Chong Kah Chun

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## **List of Abbreviations**

<u>Symbol</u>	<u>Descriptions</u>
APS	Ammonium Persulfate
CTAB	Cetyltrimethylammonium Bromide
DBSNa	Sodium Dodecylbenzenesulfonate
DMMP	Dimethyl Methylphosphonate
EDX	Energy Dispersive X-Ray
FESEM	Field Emission Microscopy
FTIR	Fourier Transform Infra-Red
HDPE	High Density Polyethylene
PEN	Polyethylene Naphthalate
PET	Polyethylene Terephthalate
PP	Polypropylene
PT	Polythiophene
PTC	Phase Transfer Catalyst
PTSA	p-Toluene Sulfonic Acid
RMS	Root Mean Squared
Rpm	Revolutions Per Minute
SDS	Sodium Dodecyl Sulphate
SEM	Scanning Electron Microscopy
SILAR method	Successive Ionic Layer Adsorption and Reaction Method
TEA	Triethanolamine
TEAp-TS	Tetraethylammonium p-Toluene Sulfonate
THF	Tetrahydrofuran
TEM	Transmission Electron Microscopy
TTAB	Tetradecyltrimethylammonium Bromide



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# **Preparation and Characterization of Electrically Conductive Plasticized Polymer-Polyethylene Terephthalate (PET) Film**

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## **Abstract**

In this study, commercially available polyethylene terephthalate (PET) was used to produce electrically conductive PET-based film. A thin layer of polythiophene (PT) film was successfully deposited on polyethylene terephthalate (PET) substrate by using simple successive ionic layer adsorption and reaction (SILAR) method. The polythiophene film deposited on PET was optimized by adjusting the monomer/oxidant molar ratio and relative thickness. The surface morphology and chemical composition of deposited polythiophene film was characterized by SEM, FTIR and EDX. The highest conductivity,  $17.905 \times 10^{-6}$  S/cm of polythiophene film achieved at monomer/oxidant of 1:3 and  $23.871 \times 10^{-6}$  S/cm during fourth coating.

**Key words:** polythiophene/polyethylene terephthalate, SILAR, electrical conductivity

## **Abstrak**

*Dalam kajian in, polyethylene terephthalate komersial yang mudah didapati telah digunakan bagi menghasilkan polythiophene yang berasaskan polyethylene terephthalate filem yang dapat mengalirkan arus elektrik. Polythiophene berasaskan polyethylene terephthalate filem telah berjaya dihasilkan melalui cara simple successive ionic layer adsorption and reaction (SILAR). Polythiophene berasaskan polyethylene terephthalate telah dioptimumkan dengan menyesuaikan monomer/oksida molar ratio dan ketebalan. Morfologi permukaan dan komposisi kimia polythiophene filem dicirikan dengan SEM, FTIR dan EDX. Polythiophene filem mempunyai kekonduksian tertinggi,  $17.905 \times 10^{-6}$  S/cm apabila monomer/oksida adalah 1:3 dan  $23.871 \times 10^{-6}$  S/cm semasa salutan kali ke-empat.*

**Kata kunci:** polythiophene/polyethylene terephthalate, SILAR, arus elektrik

## 1.0 Introduction

Over the past few decades, conducting polymer such as polypyrrole, polyaniline, polythiophene (PTh), poly(*p*-phenylene-vinylene) and poly(*p*-phenylene) have attracted great attention in many areas of modern technology due to their superior functionalities. Among this conducting polymer, polythiophene is the most promising electro-conductive polymers due to its excellent environmental stability, superior conductivity, unique photovoltaic, optical, magnetic and electronic properties (Li *et al.*, 2009; Foroutani *et al.*, 2014; Mohammadizadeh *et al.*, 2014). In addition, polythiophene in thin film form play a substantial function in several applications such as corrosion protection, sensors, super capacitors and solar cells (Tallman *et al.*, 2002; Lange and Mirsky 2011; Gnanakan *et al.*, 2009; Mohammadizadeh *et al.*, 2014). Basically, polythiophene are low in density, simplicity of fabrication, distinctive electrochemical, optical and magnetic properties. Compared to metal, implementation of electrical conductive polymers in electronic device capable to minimize the various harmful effects to human health and electronic devices due to its high electromagnetic interference shielding efficiency based on surface reflection and absorption (Wang *et al.*, 2010). However, polythiophene suffer from low conversion, low monomer reactivity, insolubility in common solvents and infusibility (Mohammadizadeh *et al.*, 2014). All these characteristics lead polythiophene to weak processability and troubles in application.

The purpose of using PET to develop electrically conductive film is because it is renewable sources and inexpensive materials which easily obtain in market. Recently, PET is widely used in various industrial applications such as packaging, medicine, automobile part and textile. Moreover, manufacturing of electronic and optical device such as LCD, electrophoretic displays, solar cell also uses PET as polymer substrate due to its light weight and flexibility (MacDonald, 2004; Mohammadizadeh *et al.*, 2014). Besides that,

there are several reports available on conducting polymer depositions on polyethylene terephthalate substrate that carried out by using in situ polymerization method. For example, polythiophene/polyethylene terephthalate conductive films, polypyrrole/polyester composite textile, polypyrrole/polyethylene terephthalate are prepared based on this approach (Erdogan *et al.*, 2012; Macasaquit & Binag., 2010; Varesano *et al.*, 2005).

Before deposition conducting polymer to polymeric substrate, surface modification is necessary to carry out. This modification will enhance adhesion of the coating and uniformity. Basically, surface modification techniques can be parted into two primary categories: chemical and physical methods. Physical methods usually use plasma, UV radiation, corona, laser, and flame. These methods modify the surface by introduce a variety of polar groups on the surface. Besides that, for chemical methods, the surface of the substrate is modified by direct chemical reaction of the reagent such as potassium hydroxide or  $\text{KMnO}_4/\text{HCl}$  (Mohammadizadeh *et al.*, 2014; Favaro *et al.*, 2007). Generally, chemical methods are non-specific as physical methods. There have various ways to transform non-conductive polymer into conductive polymers such as spin coating, dip coating, DC-magnetron sputtering, in situ polymerization, electrochemical polymerization and vapor polymerization (Ali *et al.*, 2010; Wang *et al.*, 2010; Acqua *et al.*, 2006). Different synthesis condition and dopant anion used resulted different morphology, chemical and physical properties of the film. However, some of the techniques mention above is not suitable for deposition polythiophene film, due to insolubility in the typical solution process and smooth surface morphology of PET.

In this study, the electrically conductive polyethylene terephthalate (PET) film was prepared by depositing polythiophene thin films on the PET film by simple successive ionic layer adsorption and reaction (SILAR) method. The polythiophene is chosen to coat on PET film due to its environment and thermal stability, ease polymerization process,

superior conductivity, photovoltaic and electronic properties. To accomplish this goal, the surface of PET was undergoes modification by 4M of potassium hydroxide (KOH) solution followed by SILAR method. SILAR method able overcomes the formation of unnecessary precipitates which usually resulted in chemical deposition. Thus, avoid wastage of chemical materials. The SEM, FTIR, and EDX were used for characterization and examine the surface morphology. The two probe technique was employed to evaluate the electrical conductivity of the PET film by using a digital multi-meter.

### **1.1 Problem Statement**

- How conductive polyethylene terephthalate (PET) film can be prepared?
- How the optimizing/enhance the level of conductivity of polythiophene/polyethylene terephthalate film?

### **1.2 Objectives of Study**

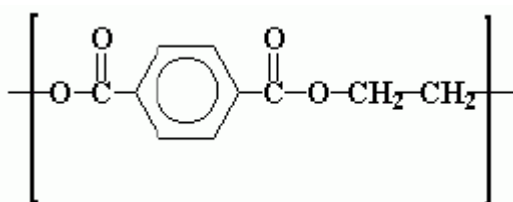
- To synthesis polythiophene (PT) film from thiophene monomer.
- To deposit polythiophene film on polyethylene terephthalate (PET) film by simple successive ionic layer adsorption reaction (SILAR) method.
- To characterize and optimize electrical conductive PT/PET film by using SEM, FTIR, EDX and multi-meter.

## 2.0 Literature Review

### 2.1 Polyethylene terephthalate/Polyethylene terephthalate film

#### 2.1.1 Molecular structure and morphology of PET

According to Reddish (1950), polyethylene terephthalate (PET) or sometime call as polyester is the first attracted attention as a possible synthetic polymer. In the year 2008, approximate 30.3 million metric tons has been produced which including both staple fibres and filament yarns (Donelli *et al.*, 2010). In general, PET is semi-aromatic and semi-crystalline thermoplastic polyester. Furthermore, PET can be prepared by condensing the polymer resulted from alcoholysis between terephthalicacidester and ethylene glycol or esterification reaction between ethylene glycol and terephthalic acid. PET is composed of repeating units as indicated in Figure 1.



**Figure 1:** Molecular structure of PET

The physical length of each repeating unit is about 1.09 nm and molecular weight is 200. Furthermore, due to its non-polar molecular structure, PET fibres only can absorb little water (Lechat *et al.*, 2006). Basically, there are two types of PET film, one is amorphous transparent material and one is a crystalline material (Amborski and Flierl, 1953). Amorphous PET film has white, opaque and brittle physical properties which crystallized by reagent (acetone) or high temperature. On the other hand, crystalline film exhibited better physical properties which are tough, tensile and flexible to temperature up to 200 °C (Amborski and Flierl, 1953). Moreover, the structural factor and orientation factor might affect the intensity of an absorption band. For examples, when PET film undergoes some crystallization process, absorption band intensity of amorphous regions will be lower

compared to the absorption band intensity of crystalline regions (Schmidt, 1963). Besides that, the proportions of crystalline and amorphous regions are depends on the way of preparation (Reddish, 1950). According to Mohammadizadeh *et al.* (2014), the surface morphology of PET film was smooth and homogenous thoroughly surfaces when observed by field emission scanning electron microscopy (FESEM). In addition, topology and the roughness of a normal PET film had a smooth surface (Favaro *et al.*, 2007).

### **2.1.2 Application of PET**

Polyethylene terephthalate (PET) has unique characteristics such as transparent, safety and lightweight, toughness, thermal resistance up to 175 °C, as well as good chemical, hydrolytic resistance (Mohammadizadeh *et al.*, 2014; Venkatachalam *et al.*, 2012). Besides that, PET fibers also exhibit superior mechanical strength, relatively high resistance to shrinkage and wear. However, undesirable properties also found in PET fibres such as hydrophobic character, static charge deposition, non-conductive and inert nature of the constituent polymer (Erdogan *et al.*, 2012; Donelli *et al.*, 2010). However, the composite PET film with conductive polymer capable to remove such undesirable properties (Erdogan *et al.*, 2012). According to Amborski and Flierl (1953), PET film has high resistance toward acid than the base. Even, at boiling point, the weak acid also does not give any effect to PET. Moreover, PET film was less affected by solvent such as glacial acetic acid, trichloroethylene, xylene, dioxane, acetone, and ethyl acetate even at room temperature or near to its boiling point. (Amborski and Flierl, 1953).



### **2.1.3 Application of PET**

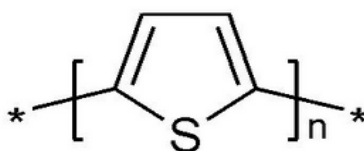
As PET has outstanding barrier properties, they usually used to make molded bottles for spirits, soft drinks, beers, pharmaceuticals and other food products. Besides that, PET films also have capability involve in various applications such as X-ray films or tapes, photographic, magnetic, metalized film and electrical insulation. Moreover, PET also have potentials to substitute aluminium, steel and other metals in manufacture of precision molding for electrical and electronic devices, automobile parts, domestic and office appliances (Venkatachalam *et al.*, 2012). The PET in fibre forms also finds uses in various applications such as thread, curtain, tire cord filaments, upholstery, wearing apparel, industrial fibres and fabric for industrial filtration. Recently, due to its unique properties, PET film involved in electronic device application and solar cell due to its flexible, light weight, and transparent properties (Mohammadizadeh *et al.*, 2014). Nevertheless, the PET also been used in the biomedical field such as Dacron (Cowie and Arrighi, 2007).

## **2.2 Conducting Polymers**

### **2.2.1 Polythiophene**

The first organic metal or conductive polymer which flexible like plastic but post-conductivity characteristics was discovered in 1977 by three scientists Shirakawa, Heeger and MacDiarmid which come from different fields (Chiang *et al.*, 1977). Conducting polymers is a chain of conjugated molecules which consists strong sigma bonding to maintain the conductive form of polymer structure. Once the oxidation of polymer was occur, the negative charged counter ion from electrolyte or oxidant would inserted and neutralized the charge balance of the bulk polymer. Electric current would be produced as the electrons are moving along the polymer chains. Examples of conducting polymer are polypyrrole, polythiophene, polyacetylene and polyaniline (Ramakrishnan, 2011).

In general, polythiophene are made up from repeating units of thiophene monomer. Polythiophene is  $\pi$ -conjugated chains with heterocyclic organic compound which generally not soluble in organic solvent due to its rigid-bone. The molecular formula for thiophene is  $C_4H_4S$  and the molecular structure is shown in Figure 2:



**Figure 2:** Molecular structure of thiophene

Polythiophene extended  $\pi$ -conjugation perfectly in 2, 5-linked repeating unit. However, 2, 3- and 2, 4-linked repeating unit also can be found in the polythiophene. Insulator polymer is non-conductive, mainly due to their electrons are localized. Polythiophene had double bond which including sigma and pi bond. The conjugated double bond and overlapping of orbital with neighbouring molecules allow the electrons delocalise along the polymer chain in giving conducting properties. Although the polythiophene was conductive, but when polythiophene doped with  $ClO_4^-$ ,  $AsF_6^-$  and  $BF_4^-$ , there shown the loss of conductivity under certain condition such as ambient atmosphere and extremely dry conditions (Nalwa, 2001). In contrast, Chiang *et al.* (1977) reported that, the polythiophene was stable in moisture and atmospheric condition.

Several advantages of polythiophene, which are ease in fabrication, low density and had distinctive electrochemical, optical, and magnetic properties. Furthermore, polythiophene was recognized as most promising materials in practical application due to their chemical stability, excellent conductivity, good thermal, tunability of their electronic and distinctive electrochemical, magnetic properties (Cheylan *et al.*, 2006). However, polythiophene also

suffer from low conversion, low monomer reactivity, insolubility in common solvents and infusibility (Mohammadizadeh *et al.*, 2014). Furthermore, the inert sulphur atom in thiophene makes the preparation of polythiophene more difficult due to increase in oxidation potential (Kamat *et al.*, 2010). So, polythiophene face difficulty in processability and troubles in application. Nonetheless, polythiophene still can play an important role in various application such as corrosion protection, sensors, supercapacitors and solar cells (Tallman *et al.*, 2002; Lange and Mirsky 2011; Gnanakan *et al.*, 2009; Mohammadizadeh *et al.*, 2014). Besides that, polythiophene also can use in fabricating electro-optical display devices. The colour changing from red to blue when voltage was applied, and this shown the possibility of polythiophene to act as optical memory element (Kumar and Sharma, 1998). In additional, conductive polymer such as polythiophene also had potential used in biochemical application (Kumar and Sharma, 1998).

## **2.3 Method of Preparation and Characterization**

### **2.3.1 Modification of PET film surface**

Surface modification technique is very important to plastics industries. As surface modification techniques had the ability to turn inexpensive synthetic polymers into highly valuable end product (Favaro *et al.*, 2007). Furthermore, substrate surface modification also can enhance the deposition process and affect conductivity of the materials. In general, surface modification techniques can be parted into two primary categories: chemical and physical methods. Physical methods were included laser, UV radiation, plasma, flame, and corona. The techniques which under physical categories often modify the surface by introduce a variety of polar groups on the substrate surface. For chemical methods, chemical reagent such as potassium hydroxide and  $\text{KMnO}_4/\text{HCl}$  was used to change the chemical nature on the substrate surface (Mohammadizadeh *et al.*, 2014; Favaro *et al.*,

2007). Nevertheless, the chemical nature on the substrate surface also can alter by covalent bonding. Generally, chemical methods are not as specific as physical methods.

Mohammadizadeh *et al.* (2014) reported that the PET film is very sensitive to alkaline; potassium hydroxide solution. Hence, the surface of the films can be modified by the alkaline modifying agent such as potassium hydroxide (KOH). After modification, the films wash several times with deionized water and dried with N<sub>2</sub>. Besides, stirring the KOH solution without contact with the PET film by using magnetic stirrer can ensure the PET film are evenly modified. Thus, increase the surface hydrophilicity and evaluated by water contact angle measurement. Aqueous KOH solution can causes etching, increase the porosities of substrate, and introducing polar group on the PET surface, so that suitable for mechanical locking and physical bonding with the polythiophene nanoparticles on PET (Mohammadizadeh *et al.*, 2014).

Besides that 4M of the KOH, four different surfaces modify agent such as 12M KOH, Piranha solution, UV, combination of Piranha solution and UV had use to modify the surface morphology of polyethylene naphthalate (PEN) (Foroutani *et al.*, 2014). According to Foroutani *et al.* (2014), piranha solution is an oxidizing mixture which made up by different ratio of sulphuric acid and hydrogen peroxide. The substrate was modified at room temperature and elevated temperature (at 65 °C) by dipped in 20 ml concentrated sulphuric acid (95-98%) and 10 ml hydrogen peroxide (30%) for different periods of immersion time (5, 15, 30 min and 1 h). Foroutani *et al.* (2014) reported that, the alkaline KOH treatment leads to loss in optical transparency up to 84% and not significant increase in surface hydrophilicity of polyethylene naphthalate (PEN). However, Piranha solution significantly affects the surface morphology of PEN and gives less effect on PET film. Among several different methods that used in surface modification, irradiation by UV are the preferred modification method and made up conductivity 0.019 S/cm. Whereas, KOH

surface treatment for PEN film only contribute conductivity with 0.004 S/cm (Foroutani *et al.*, 2014).

According to Gao *et al.*, (2005), PET film undergoes surface modification via hydrolysis reaction. The PET is hydrolysis by concentrate alkaline solution, and follow by layer-by-layer assembly of chitosan and chondroitin sulfate on PET film. The surface modified PET film produce carboxyl group by cleavage of the ester groups. As the hydrolysis process will cause weight loss in molecular level, so the hydrolysis process was stopped once sufficient hydrophilicity achieved (Gao *et al.*, 2005). Besides that, the change surface morphology determined by atomic force microscopy (AFM) imaging. The surface morphology PET film became very rough (RMS=37.9nm) after hydrolyzed for 35 min compared to untreated PET film (RMS=11.9nm) (Gao *et al.*, 2005).

Besides alkaline solution, surface modification also can accomplish by using the oxidative acid solution. According to Favaro *et al.* (2007),  $\text{KMnO}_4/\text{HCl}$  solution was employed to change the surface morphology of poly (ethylene terephthalate) (PET), polypropylene (PP), high-density-polyethylene (HDPE) and films by varying the time, oxidative solution, and temperature. Favaro *et al.* (2007) had reported that, two competitive reactions occur in PET films, oxidative and hydrolysis reactions which affect the hydrophilicity result that expected from PET films. However, the surface morphology of PET films did not change significantly after treating with  $\text{KMnO}_4/\text{HCl}$  solution. This was due to hydrolysis only occur after removed the changed polymer or clean the PET film surface (Favaro *et al.*, 2007).

Besides KOH, NaOH also used increase the roughness of PET surface (Tho and Ibrahim, 2012). Tho and Ibrahim (2012) reported that, the surface roughness was due to alkaline hydrolysis and resulted caboxylate-functionalized PET surface that cause imperfections on

the surface. Besides that, the longer the treatment time, higher concentration of NaOH and higher temperature of the reaction, the better the PET surface modification. In high temperature, the hydrolysis reaction is easier to perform due to hydrogen bonding interaction in the polymer are weakened. Moreover, high concentration NaOH increases the chance of collision, thus increasing the rate of reaction. According to the Tho and Ibrahim (2012), among the factor, the concentration was significantly influence the roughness of the PET which increase from 6.025nm to 16.700nm by using 0.25M and 1M NaOH. On the other hand, once the PET was chemically treated, the PET surface change from uniform, small hills and deep cavities, larger hill and deep cavities respectively (Tho and Ibrahim, 2012).

### **2.3.2 Preparation of electrically conductive polymer films**

A ‘film’ can be defined as a layer of material on a supporting substrate. If there is no supporting substrate, it is known as a foil. Moreover, compare to bulk materials, film has its special properties certain conditions. In general, there are a lot of techniques to synthesis conductive polymer such as chemical polymerisation, electrochemical polymerisation, photochemical polymerisation, concentrated polymerisation, solid-state polymerisation, plasma polymerisation, soluble precursor polymer preparation, inclusion polymerisation, and metathesis polymerisation. However, among all the techniques, chemical polymerizations are the most useful in preparing large quantities of conductive polymers (Kumar and Sharma, 1998). In chemical polymerization, the monomers were oxidized into cation radical and their coupling to form di-cations radical and this process was repeated and generates a polymer (Kumar and Sharma, 1998).

On the other hand, there are various studies from different approach in the synthesis of polythiophene particles or films. Polythiophene film was prepared in glass substrate by

simple successive ionic layer adsorption and reaction (SILAR) method (Patil *et al.*, 2012). The iron(III) chloride acts as oxidant in this oxidative polymerization. The  $\text{FeCl}_3$  in ultrapure water act as anionic precursor, whereas the thiophene in acetonitrile acts as cationic precursor. This reaction was carry under acidic medium (pH 1). Firstly, the glass substrate was immersed in the thiophene solution for 20 second to allow thiophene adsorbed on the glass. After that, immersed in  $\text{FeCl}_3$  solution for 10 second to allow the polymerization occurs in the surface of the glass. The polymerization would yield a polythiophene thin film in the surface of glass and capable applies in super-capacitor applications. The mechnism involve during SILAR method initial with the oxidation of thiophene to form cationic radical (Reyman *et al.*, 2007). The resulted cationic radical was coupling each other to form dihydrodimeric dication and undergoes deprotonation to form dimer. As dimer is more easily undergoes oxidation compared to thiophene. Thus, the dimer being keep repeating the oxidation, coupling and deprotonation reaction and eventually polymerize into polythiophene (Patil *et al.*, 2012). Besides that, Can *et al.*, (1998) reported that the purpose of providing acidic condition when electro-polymerization of polythiophene is to stabilize the formation of cation radicals. In contrast, if the electro-polymerization process carries under neutral and base condition, the resulted film would significantly reduce due to the de-protonation reactions of the cation radicals of thiophene monomer and polymers (Can *et al.*, 1998).

According to Pecher and Mecking (2010), oxidation of  $\text{FeCl}_3$  with catalytic amount of  $\text{H}_2\text{O}_2$  have a better result than iron(III) salts as the sole oxidant. This is because the iron in the salt can deteriorate the photoluminescence properties (Ryu *et al.*, 2014). Furthermore, Wadtkar and Waghuley (2012) reported oxidation of  $\text{FeCl}_3$  in the presence of  $\text{H}_2\text{O}_2$  capable speed up the reaction and increase the yield. Pecher and Mecking (2010) also found out that, surfactant such as sodium dodecyl sulfate (SDS) are the most efficient in

monomers conversion which as high as 99% if the  $\text{FeCl}_3$  as oxidant. This is because electrostatic interactions between SDS and  $\text{Fe}^{3+}$  which allow  $\text{Fe}^{3+}$  come near to the swollen droplets or micelles during polymerization. So, irregular shape of polythiophene particles approximate 30nm were obtains. Furthermore, the presence of surfactant will decrease the agglomeration of the polythiophene (Senthilkumar *et al.*, 2011). Thus, polythiophene particles were stabilized. On the other hand, different morphology of polythiophene will exhibit when samples prepared with surfactant compared with surfactant free samples.

Other than that, polythiophene was synthesized by chemical oxidative polymerization in the presence of oxidant ( $\text{FeCl}_3$ ) and three different surfactants (non-ionic, anionic, and cationic) in an anhydrous medium (Gok *et al.*, 2007). The presence of anionic surfactant (DBSNa) favours the formation of thiophene radical-cation and subsequent polymerization to occur. Whereas, the cationic surfactant (TTAB) shown not efficiency in the production of thiophene radical-cations and slows down polymerization process (Gok *et al.*, 2007).

Based on Liu and Liu (2009) study, polythiophene was prepared in the presence of phase transfer catalyst such as cetyltrimethylammonium bromide (CTAB) in aqueous medium by chemical oxidative polymerization. Desire morphologies of polythiophene which include ribbons, fibre and spherical form were obtained by simply manipulation on the concentration of oxidant, reductant, and phase transfer catalysts. The conductivity increase as the concentration of triethanolamine increased, and the morphology of polythiophene was changed from spherical shape to submicroribbons (Liu and Liu, 2009). Besides that, shown that polythiophene prepared by chemical oxidative polymerization was the most stable method compared to previous work.

Unsubstituted polythiophne was synthesized in binary organic solvents of acetonitrile and dichloromethane through facile and rapid chemical oxidative polymerization method (Jeon



*et al.*, 2010). Same method implemented by Mohammadizadeh *et al.* (2014) but addition of surfactant (CTAB) was added to obtain specific nanoparticles morphology. In order to make comparison, unsubstituted polythiophene was synthesized in two other mediums: acetonitrile and aqueous mediums. The unsubstituted polythiophene synthesis in binary organic solvent under  $\text{FeCl}_3$ /thiophene monomer molar ratio 5:1 and reaction time are 0.2 h at 0 °C condition, exhibited the highest electrical conductivity ( $20.1 \text{ Scm}^{-1}$ ). Whereas, the unsubstituted polythiophene synthesized in acetonitrile mediums exhibit low electrical conductivity ( $1 \times 10^{-4} \text{ Scm}^{-1}$ ). Furthermore, the full amorphous structure of brown polythiophene was synthesized through aqueous medium and exhibit neutral non-conducting property (Jeon *et al.*, 2010). This is due to the thiophene ring attacked by nucleophilic water molecules.

According to Li *et al.* (2009), fine polythiophene microparticles were synthesized by a novel interfacial polymerization which contains oxidant and thiophene at binary solvent such as acetonitrile and n-hexane. Li *et al.* (2009) had reported that, oxidant concentration significantly affects electrical conductivity. As the  $\text{FeCl}_3$ /thiophene molar ratio change from 2:1 to 6:1, the conductivity increase from  $5.2 \times 10^{-9}$  to  $1.7 \times 10^{-7} \text{ Scm}^{-1}$ .

Mohammadizadeh *et al.* (2014) had carried out a research to study the deposition of polythiophene (PT) nanoparticles on transparent polyethylene terephthalate (PET) and how the electrical and morphological properties were influenced. The surface PET film was modified by modifying agent (KOH) and immerse in thiophene monomer solution to undergo polymerization. According to Mohammadizadeh *et al.* (2014), polythiophene nanoparticles successfully deposited on polyethylene terephthalate film by a oxidative deposition method using the binary organic solvent system in the presence of N-cetyl-N,N,N-trimethylammonium bromide (CTAB) as cationic surfactant. In addition, water are not suitable in oxidative polymerization of thiophene, due to possible incorporation of

carbonyl groups into the structure of the polymer (Li *et al.*, 2009). The PET film undergoes alkaline (KOH) surface treatment, then followed by polymerization and deposition of conducting polythiophene on PET surface. When PET was treated with KOH solution, the PET film undergoes chemical alternation, which leads to formation of polar groups on its surface and complements the physical bonding and become porosities. The polymerization allows proceed for 12 min and deposition of polythiophene on PET surface would occur. In this polymerization process, the CTAB must vigorously stir to ensure the yield of polythiophene. This is because stirring makes the nanoparticles that trapped in CTAB become well dispersed in solution (Li *et al.*, 2009). Besides that, a similar method of deposition was adopted on PEN films (Foroutani *et al.*, 2014). Besides polythiophene nanoparticles film mention before, polythiophene film with size between 2-3  $\mu\text{m}$  also can prepared through electrochemical polymerization onto a carbon paper substrate by galvanostatic method in an oil-in-ionic liquids micro-emulsion electrolyte (Zhang *et al.*, 2014).

The effect of different synthesis conditions on the electrical conductivity of polypyrrole coated polyethylene terephthalate fabrics also been study by Kaynak and Beltran (2003). Parameters such as the time, temperature and molar concentration of the reactant of the reactants had a substantial influence on the resultant conductivity, and the rate or the ratio of volume to surface polymerization. Besides, in order to get a higher conductivity, conductive film of greater resistance to abrasion were required, and synthesis needs to be conducted in low temperature (Kaynak and Beltran, 2003). Mohammadizadeh *et al.* (2014) also reported that several factors affect the deposition of PT nanoparticles and conductivity such as polymerization media influence, the presence of water in the solution, oxidant/monomer molar ratio. The conductivity can be increased by reducing the time of the polymerization process (<5min). This is because, when the polymerization process was

increased, the side reaction also increased. Besides that, the PET films were immersed in  $\text{FeCl}_3$  solution or thiophene monomer solution for several hours up to 24 hours. This step will increase the amount of polythiophene that adhered on the PET film. In addition, uniformity of deposit polythiophene with dense packing of the particles is one of the factors that ensure high conductivity (Foroutani *et al.*, 2014). According to Kelkar & Choursia (2011), polythiophene had been synthesized chemically. Kelkar & Choursia (2011) also reported that the content of sulphur (S) in polythiophene decrease as the doping duration of iron (III) chloride increases. This phenomenon is subject to the formation of complex between iron (III) chloride and S in polythiophene, and replacement of S by  $\text{Fe}^+$  after doping. Besides that, the conductivity of polythiophene film increase as the amount of dopant increase. However, the reduction product of  $\text{FeCl}_2$  remains in the film lead to 'dedoping' of film and increase effect on stability of polythiophene film (Fichou, 1999). Furthermore, the thickness of polythiophene film must thinner than  $10\mu\text{m}$  in order to achieve high strength, stiffness and quality (Feng, 2002).

According to Kumat *et al.* (2010), the polythiophene thin film was prepared by vacuum evaporation technique. The surface morphologic, electrical, optical and structural properties were strongly affected by post heating deposition. At high temperature, the electrical conductivity of post heated polythiophene increase exponentially due to modification of structural characteristics of the polythiophene film (Kumat *et al.*, 2010). Although various solvent capable to dissolve the thiophene monomer in order for polymerization to occur. But, the presence of dangerous solvent in the film will bring many unfavourable conditions to being use in certain fields. So, another polythiophene synthesis method (plasma polymerization) had been introduced by Wen *et al.* (2014). The polythiophene-like thin films was prepared by manipulating the pressure, power as well as doping with iodine vapour in order to get high conductivity film (Wen *et al.*, 2014).

### 2.3.4 Characterization of electrical conductive polymer films

According to Seyam *et al.* (2015), electrical resistance can be defined as the ability of a material to resist the flow of electrons when voltage was applied between two contact points on the materials. Whereas, the electrical conductivity is inversely proportional to the electrical resistance as equation shown below:

$$\text{Conductivity} = 1 / \text{Resistivity}$$

The conductivity of polythiophene significantly affected in the presence of surfactant (Gok *et al.*, 2007). Among three different surfactant, poly(ethylene oxide)(20), tetradecyltrimethylammonium bromide (TTAB), and sodium dodecylbenzenesulfonate (DBSNa), polythiophene prepared by poly(ethylene oxide)(20) exhibit the highest conductivity,  $4.6 \times 10^{-4} \text{ Scm}^{-1}$  (Gok *et al.*, 2007). The high conductivity might be due to the poly(ethylene oxide)(20) surfactant interacted with polythiophene chains. Whereas, the polythiophene thin film prepared through SILAR method exhibit electrical resistivity as high as 484  $\Omega\text{-cm}$  at room temperature (Patil *et al.*, 2012). Apart from that, Kamat *et al.*, (2010) also shown the effect of temperature on the electrical conductivity of polythiophene thin films. As the temperature increase the electrical conductivity decrease and again increase at 400K. This might due to the removal of impurities such as solvent molecules or absorbed gases. According to Kattimani *et al.* (2014), polythiophene was synthesized at three different temperatures by chemical oxidative technique with ferric chloride as an oxidizing agent. The conductivity of polythiophene (3 replicate) obtained at room temperature are  $2.43 \times 10^{-5} (\Omega\text{m})^{-1}$ ,  $0.95 \times 10^{-5} (\Omega\text{m})^{-1}$  and  $1.65 \times 10^{-5} (\Omega\text{m})^{-1}$  respectively (Kattimani *et al.*, 2014). Moreover, Mohammadizadeh *et al.* (2014) report shown PT nanoparticles are deposited as globular aggregates with an average size of about 50nm on PET and conductivity is  $1.18 \times 10^{-2} \text{ S/cm}$ .

Scanning electron microscopy (SEM) or field emission microscopy (FESEM) was used to investigate the surface morphology of sample. Before proceeding to SEM, the appropriate disk was prepared to place the fabric and the fabric was copper-sputtered prior to observation (Wiener *et al.* 2013). According to Li *et al.* (2009), the morphology of polythiophene nanoparticles were almost spherical or ellipsoidal particles with similar size when observed by field-emission SEM. The reason for not all the nanoparticles in spherical shape was because during polymerization, CTAB was unable to form stable micelles in the two-phase system (Li *et al.*, 2009). In contrast, the polythiophene film prepared by oxidative polymerization shown a uniform and smooth surface morphology with randomly distributed coalesced grains in SEM micrograph (Patil *et al.*, 2012; Kamat *et al.*, 2010). Furthermore, almost spherical polythiophene nanoparticle was aggregated to produce globular morphology on PET surface when observed by using FESEM (Mohammadizadeh *et al.*, 2014).

Jeon *et al.* (2010) also reported, different polymerization medium strongly affect the morphology of polythiophene. In binary organic solvent medium, the aggregated ellipsoidal unsubstituted polythiophene nanoparticles (50-200 nm) was observed by using SEM and TEM. A bulky shapeless unsubstituted polythiophene nanoparticles microstructure are observed in acetonitrile medium and globular morphology with particles size range of 30-70nm was observe in aqueous medium (Jeon *et al.*, 2010). Moreover, the temperature of polymerization will induce more and more site of reactions. Thus, yields the formation of unsubstituted polythiophene nanoparticles with low conductivity (Jeon *et al.*, 2010). Besides that, the surface morphology of polythiophene prepare in the presence of tetradecyltrimethylammonium bromide surfactant are in layered structure (Gok *et al.*, 2007). If the particle produces were small enough, TEM analysis was carried out to confirm the particles sizes and agrees the size particles and distribution from capillary

hydrodynamic fractionation (Pecher and Mecking, 2010). Apart from that, different morphology of polythiophene particle or film can be observed according to different approaches such as time of polymerization, temperature, solvent, presence of surfactant and other influences (Senthilkumar *et al.*, 2011).

FTIR was used in the examination of the chemical composition of the polythiophene/PET film (Mohammadizadeh *et al.*, 2014). The sample was ground into powder and turns into a pellet by mixing with KBr before FTIR analysis. By referring to FTIR spectrum polythiophene nanoparticles deposited on the PET substrate in binary solvent. The peak shown at 727 and 793  $\text{cm}^{-1}$  is due to C-S stretching vibration mode of the thiophene ring (Mohammadizadeh *et al.*, 2014). Besides that, the absorption band at 683  $\text{cm}^{-1}$  represents the C-S-C planar deformation of the thiophene ring (Kamat *et al.*, 2012). The C=C asymmetric vibration mode of the thiophene ring will lead to appearing of peak at 1622  $\text{cm}^{-1}$  (Kamat *et al.*, 2012). The strong peak exhibit at 1734  $\text{cm}^{-1}$  is due to steric group (-CO-O-) of PET substrate (Mohammadizadeh *et al.*, 2014). Moreover, the bands at 2930.87  $\text{cm}^{-1}$  and 3399.46  $\text{cm}^{-1}$  are due to the aliphatic C-H stretching vibration and O-H stretching of water (Patil, *et al.* 2012). Besides that, the absorption peak about 3429 and 2864  $\text{cm}^{-1}$  are represent the O-H stretching vibration of water in KBr and aliphatic C-H stretching vibration respectively (Zhang *et al.*, 2014).

## **2.4 Application of electrical conductive polymer films**

Collins and Buckley (1996) reported that, the conductive polymers such as polypyrrole or polyaniline has been coated onto PET or nylon threads woven into a fabric mesh by spraying or dip-coating. The chemical sensing properties of conductive polymers coated onto woven fabric materials capable to act as the detector of toxic gases such as dimethyl methylphosphonate (DMMP), nitrogen dioxide, chemical warface simulant, and ammonia.

According to Wang *et al.* (2010), electrical conductive polymer films can act as electromagnetic interference shielding materials. As the metal or metal coated surface, usually has a high EMI shielding efficiency based on surface reflection, which gives harmful effect to human body and prevent some sensitive electronic device to operate. So, metal is not ideally used in some application (Wang *et al.*, 2010). Textiles coated with conductive polymers not only reflect but also able to absorb the electromagnetic waves. It has wide potential application in the military (camouflage material), industry (shielding EMI), and blocking electromagnetic wave from daily life (Kuhn, 1997). Besides that, conducting electro-active polymers also involved in various application fields such as antistatic coatings, batteries, metallization of dielectrics, shielding of electromagnetic interferences, sensor and sensor arrays (Wang *et al.*, 2010). Other than that, the polythiophene also bring advantages in application of field effect transistors (FET) compared germanium and silicon due to its low cost and ease of processing (Ates *et al.*, 2012).

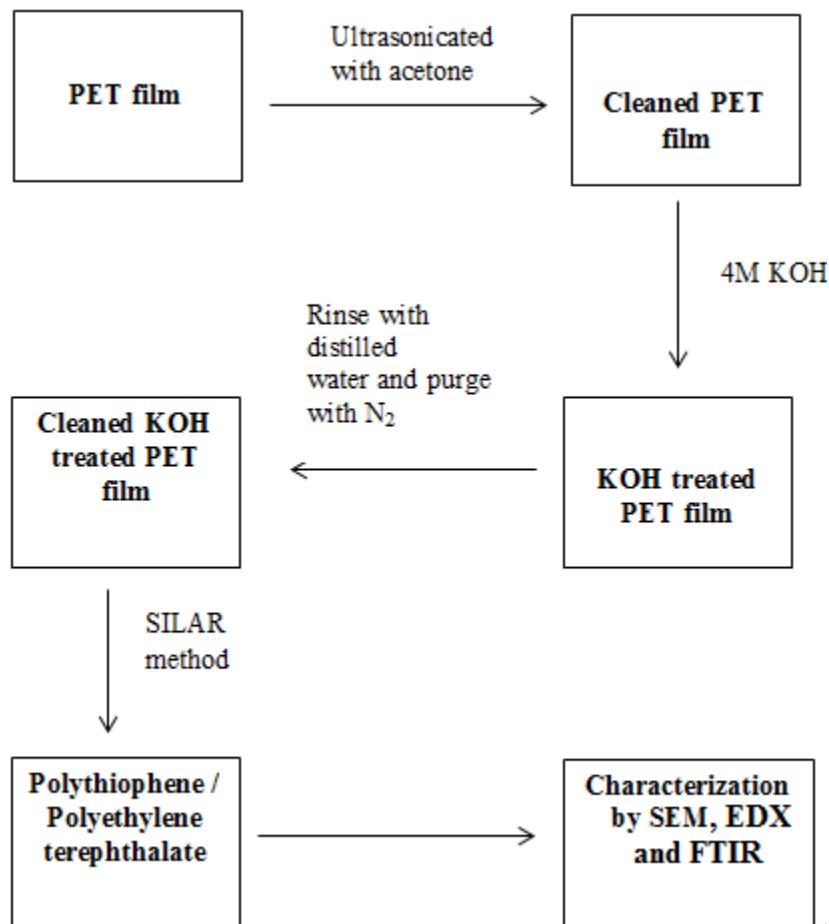
On the other hand, transparent electrodes based on conducting polymers also play an important role in display application (Chu *et al.*, 2013). According to Youssef *et al.* (2012), conductive paper composites based on natural cellulosic fibres have potential use as anti-bacterial paper or anti-static packaging material for packaging application. This new composite is made up via *in situ* emulsion polymerization from unbleached bagasse or rice straw fibres and polyaniline (Youssef *et al.*, 2012). Besides that, conductive PET film also play important role in antistatic application. New antistatic film had been developed by coating conductive polymer, sulphonated polyaniline and water dispersible polymer (Konagaya *et al.*, 2002). The antistatic PET film offer a lot of advantages such as good transparency, superior antistatic properties, resistance to heat, water and ammonia (Konagaya *et al.*, 2002).

According to Onoda *et al.* (2009), conductive polymer/insulating polymer composite films were used to evaluate biocompatibility in neuron cultures. Onoda *et al.* (2009) reported that, polypyrrole and poly(3,4-ethylenedioxythiophene) film can be used to support secretory functions of the cells which cultured on its surface. If biocompatibility was excellent in this application, then, to realize bioelectronics would be possible (Onoda *et al.*, 2009). Besides that, graphene nanoribbon/polyaniline composite film, which was prepared via electro-polymerization method and played significant role in electrochemical detection of dobutamine (Asadian *et al.*, 2014). The graphene nanoribbon/polyaniline composite film was used as an electrode modifier to construct a sensing platform to investigate dobutamine. This composite film was useful, especially in pharmaceutical and clinical preparations (Asadian *et al.*, 2014).



### 3.0 Materials and Methods

#### 3.1 Preparation and treatment of PET films

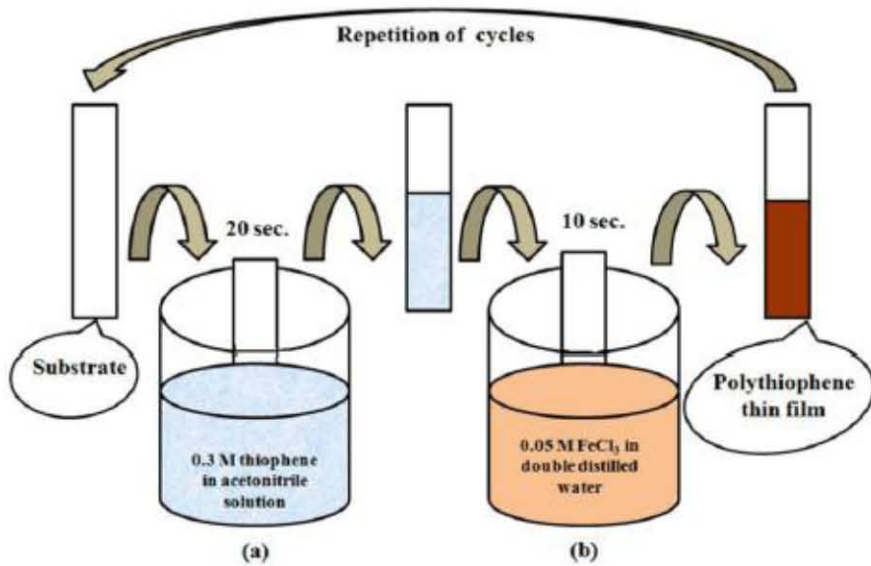


**Figure 3:** Overall of methodology used for the preparation and characterization of electrically conductive PET-based films.

Figure 3 show a flow chart of an overview of methodology used in this study. The PET film was provided by UNIMAS physical chemistry laboratory. The PET film was cut into 1 cm × 4 cm pieces and ultrasonicate with acetone. After sonication, the cleaned PET films was immersed in 4M aqueous KOH for 4 hours at 80 °C by using thermostatic water bath for surface modification. After the modification, the substrate was rinsed with plenty of distilled water several times and blown dry by using nitrogen gas (Mohammadizadeh *et al.*, 2014).

### 3.2 Preparation of electrically conductive polythiophene/PET-based films

In the first beaker, 0.3 M thiophene was dissolved in 10 ml of acetonitrile which acts as a cationic precursor with pH 1. The second beaker, 0.9 M  $\text{FeCl}_3$  was dissolved in 10 ml of ultrapure water and acts as an anionic precursor. The cleaned PET film was dipped into the cationic thiophene for 20 seconds which allows the thiophene to adsorb on the PET surface and followed by 10 seconds in  $\text{FeCl}_3$  solution. The thickness of the polythiophene film was increased by repeated SILAR cycles and the resistivity value was measured. (Patil *et al.*, 2012). Different monomer and oxidant ratios; monomer:oxidant = 1:2; 1:3; 1:4; 1:5 respectively were manipulated in order to optimize the conductivity. A simple illustration of the SILAR method procedure was shown in Figure 4.



**Figure 4:** Illustration of SILAR method for deposition of polythiophene on PET film (Patil *et al.*, 2012)

### **3.3 Characterization of Electrically Conductive PET-based Film**

#### **3.3.1 Physical Characterization**

##### **a.) Surface morphology (Scanning electron microscopy)**

The surface morphology of the original PET film, treated PET film, polythiophene (PT), and PT/PET based film was observed by using scanning electron microscopy (SEM) (JEOL JSM-6390LA) with magnification of 5000x and 10000x. Before proceeding to SEM examination, the sample surface was placed on an appropriate plate and coated by Auto Fine Coater JEOL JFC-1600.

##### **b.) Conductivity measurement (Digital multi-meter)**

The surface resistivity of sample film was measured by using the two probe technique with a digital multi-meter. The average of measurements was randomly takes from five different regions with fixed distance (1 cm) in the sample film. Then, the average surface resistivity was converted into the conductivity by equation below:

$$\text{Conductivity} = 1/\text{Resistivity}$$

#### **3.3.2 Chemical Characterization**

##### **a.) Chemical composition (Fourier transform infra-red spectroscopy)**

The chemical structure and composition of electrically conductive PT/PET films were determined by using Fourier Transform Infra-red Spectroscopy (FTIR) (Thermo Scientific/Nicolet iS10) within the range of  $400\text{cm}^{-1}$  to  $4000\text{cm}^{-1}$ . The polythiophene film that deposited on the PET film was scratched and mixed with KBr to form pellet for infrared measurements

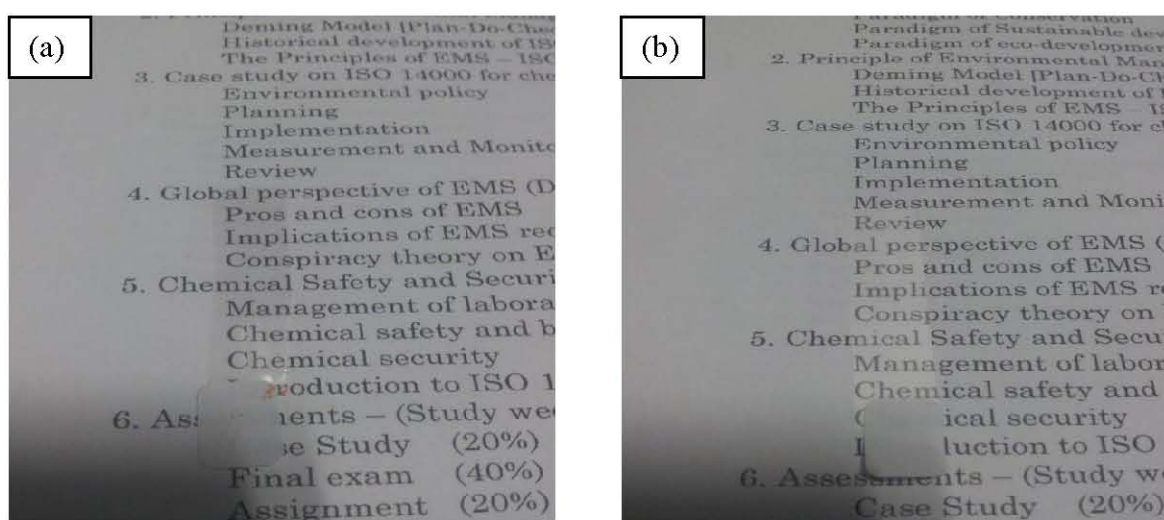
##### **b.) Elemental analysis (Energy dispersive X-Ray spectroscopy)**

The presence of polythiophene on PET film was determined by using EDX. The presence of element such as carbon (C), and sulfur (S) confirm the presence of polythiophene.

## 4.0 Results and Discussion

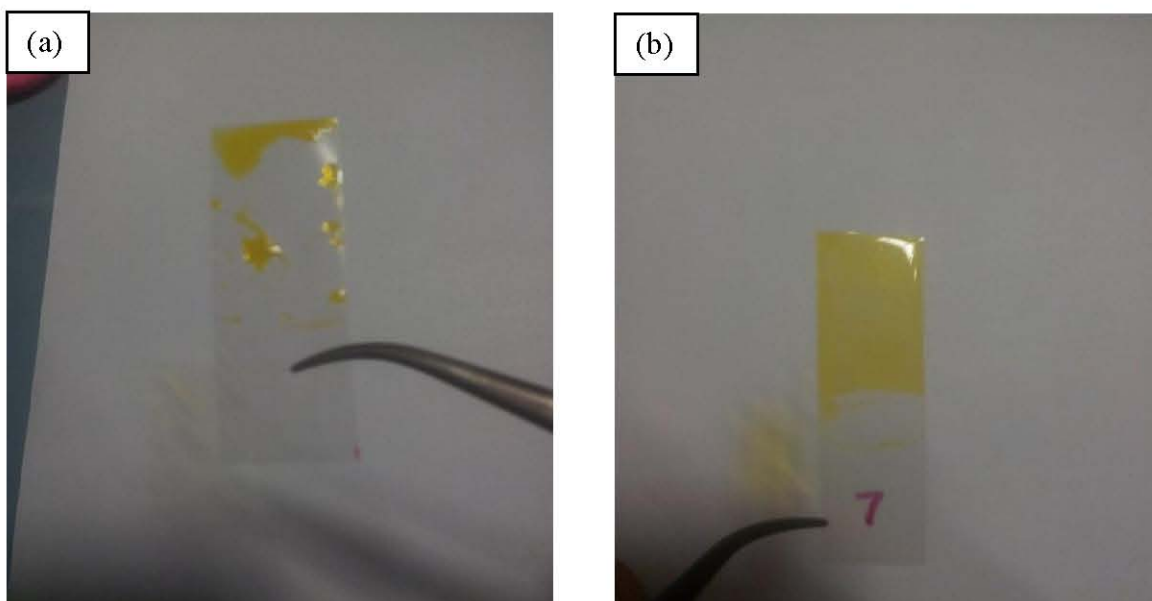
### 4.1 Surface modification of Polyethylene Terephthalate (PET) film

The PET films were ultrasonicated with acetone to physically remove and dissolve any impurities on the PET surface. The potassium hydroxide (KOH) surface treatment changes the hydrophilic and roughness of PET films surface. In order to evidence the observed decrease in transparency, images of untreated PET film and KOH treated PET film are shown in Figure 5. Obviously, the transparency of KOH treated PET film was decreased.



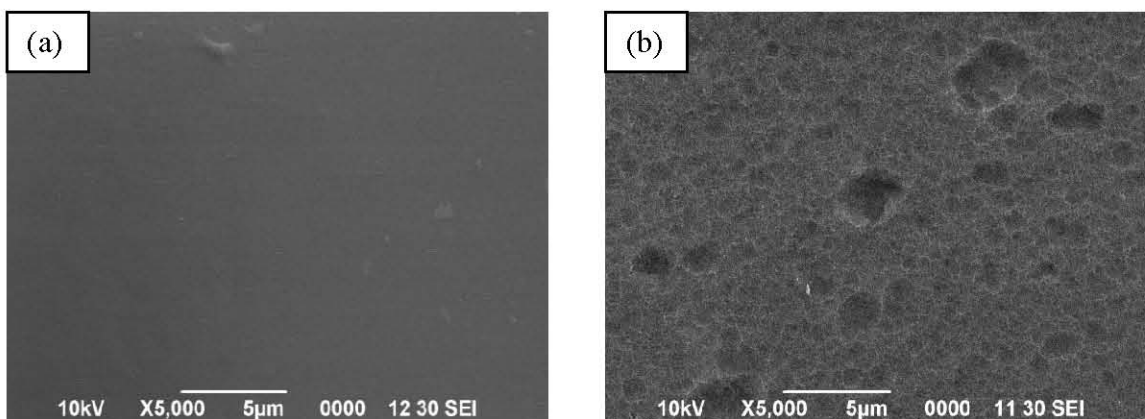
**Figure 5:** Images of untreated PET film (a) and KOH treated PET film (b).

The ultimate purpose of surface modification was to increase the adhesion of polythiophene thin film on PET film. As shown in Figure 6, the polythiophene thin film resulted from the polymerization process was observed to adhere well onto KOH treated PET compared with the untreated PET. Besides that, the increase PET roughness was observed in the SEM micrographs as shown in Figure 7.



**Figure 6:** Images of polythiophene thin film deposited onto (a) untreated PT/PET film, and (b) KOH treated PT/PET film.

#### 4.1.1 SEM Characterization



**Figure 7:** SEM micrograph of (a) untreated and (b) treated PET films (4 M KOH, 4 hours).

Figure 7 shows the SEM micrograph of untreated PET film and KOH treated PET film at 5000x magnification. The surface morphology of untreated PET film was observed to be smooth and uniform. In contrast, KOH treated PET film showed substantially large and deep cavities. The surface roughness of PET (Figure 7 (b)) was due to surface degradation of PET film. The aqueous KOH solution creates porosities that favour the mechanical

locking of the PT on PET film. Moreover, the aqueous KOH also cause chemical alternation of the PET surface by introduction of polar group which resulted van der Waals forces become the main forces for physical bonding and interactions (Mohammadizadeh *et al.*, 2015).

## **4.2 Electrically conductive polythiophene/PET-based films**

### **4.2.1 Polythiophene/PET-based film**

Figure 8 shown the image of the polythiophene/PET-based film which synthesized via SILAR method in room temperature. As shown in Figure 8, a layer of brownish polythiophene which completely adhered on the PET film.



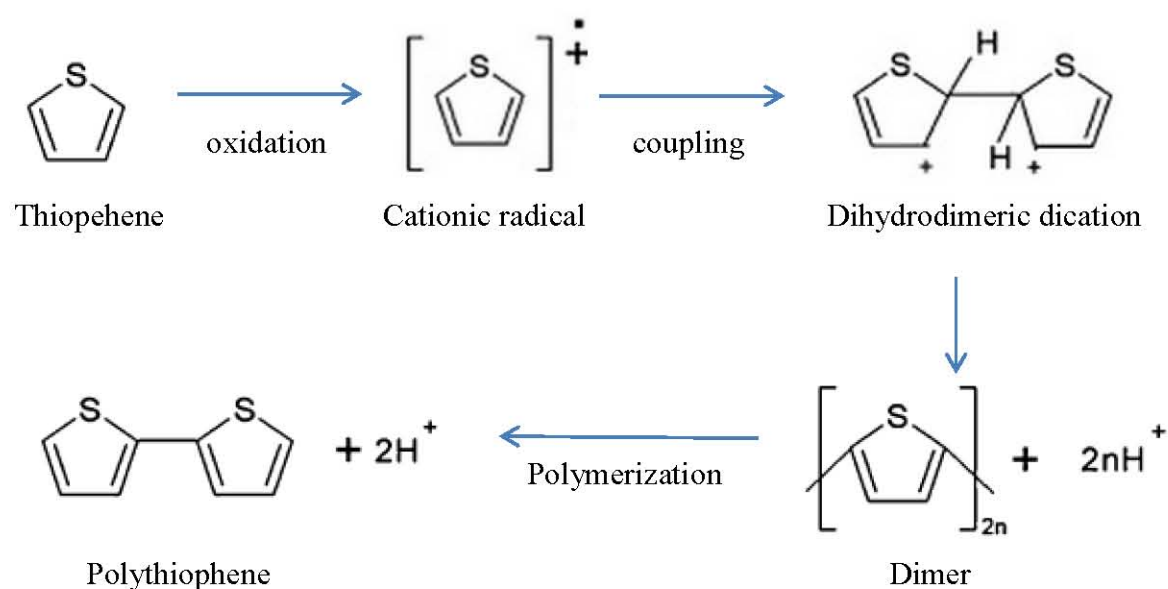
**Figure 8:** Image of polythiophene/PET-based film synthesized via SILAR method.

### **4.2.2 Formation of polythiophene/PET-based films**

The polythiophene films were obtained using successive ionic layer adsorption and reaction (SILAR) method at room temperature (Patil *et al.*, 2012). The polymerization occurred when the monomer with the radical cation was oxidized by iron(III) chloride,  $\text{FeCl}_3$ . When a cleaned PET film was dipped into the thiophene solution, the thiophene was

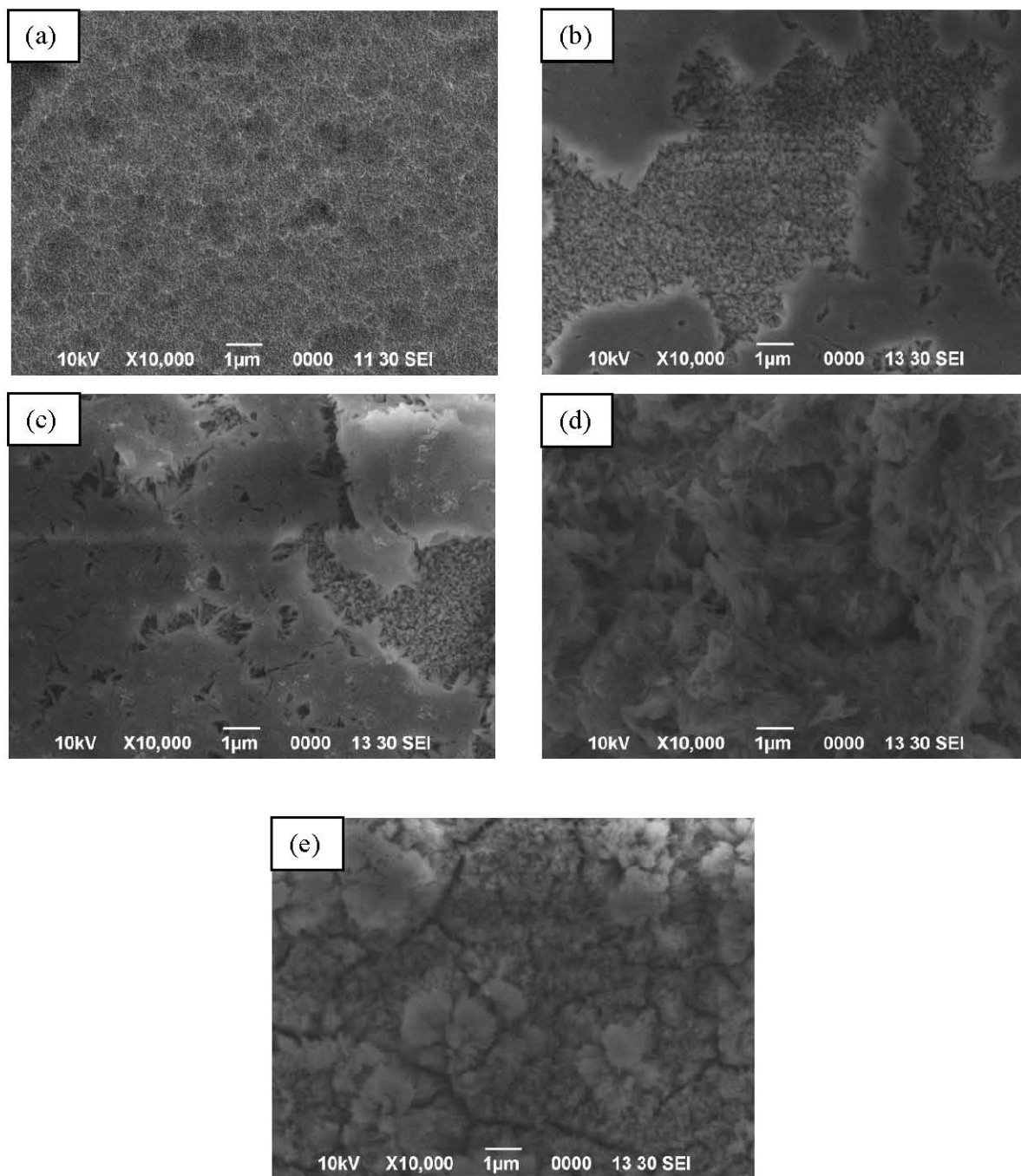


adsorbed onto the PET surface. Once the adsorbed thiophene was further dipped on the the  $\text{FeCl}_3$  solution, the thiophene underreact oxidation to form cationic radical (Reyman *et al.*, 2007). The resulted cationic radicals were coupling with each other to form dihydrodimeric dication and underreact deprotonation to form dimer. As dimer is more easily undergoes oxidation compared to thiophene, the dimer continually repeating the oxidation, coupling and deprotonation reaction, and eventually polymerized into polythiophene. Besides that, cationic precursor was maintained at pH 1 to providing acidic medium which act to stabilized the formation of radical cation. The reaction mechanism for the formation of polythiophene from thiophene is shown in the Scheme 1:



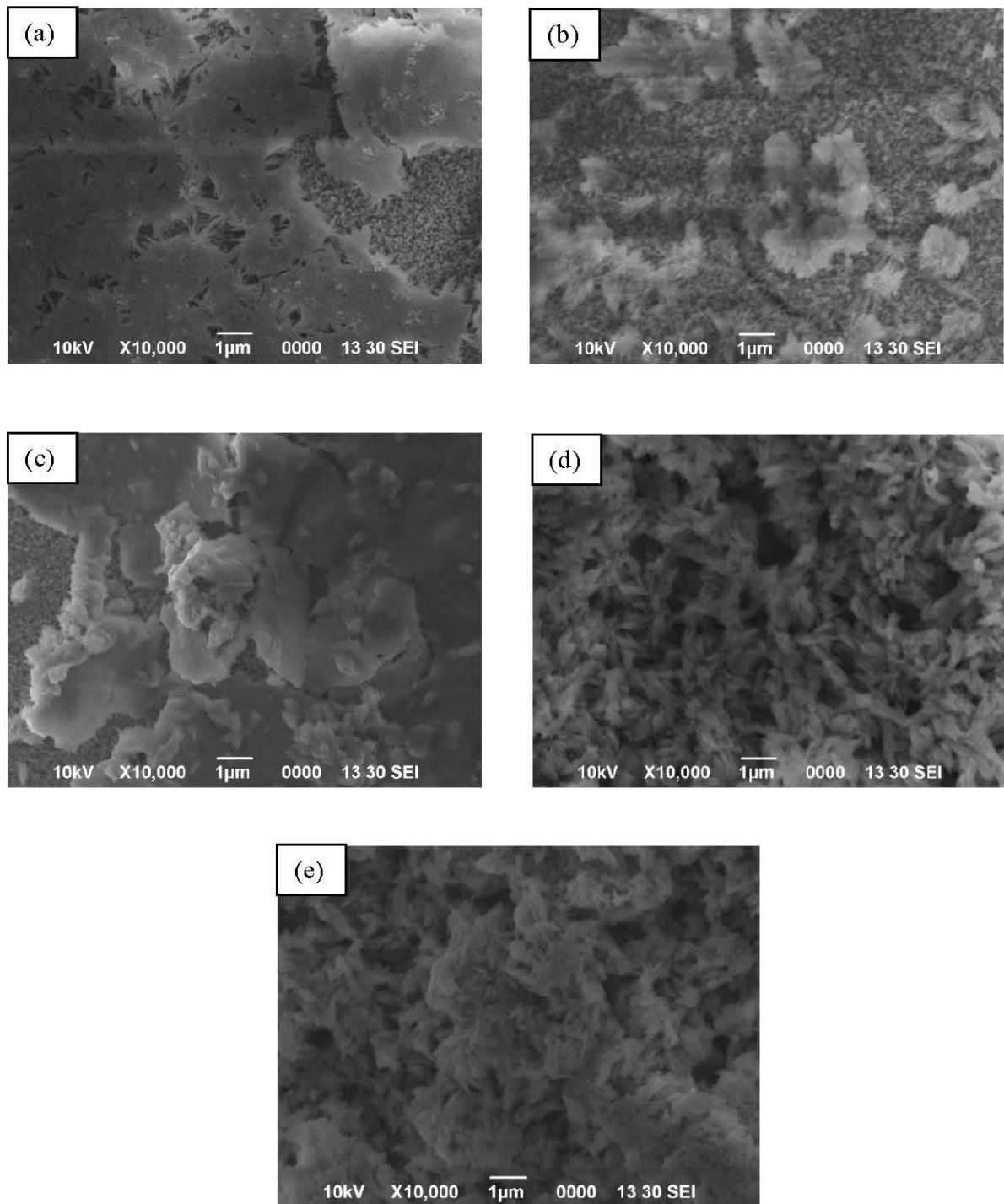
**Scheme 1:** Reaction mechanism for the formation of polythiophene from thiophene

### 4.2.3 Scanning Electron Microscope (SEM)



**Figure 9:** SEM micrographs of PT film on PET deposited by the SILAR method, (a) KOH treated PET surface, and monomer/oxidant of (b) 1:2, (c) 1:3, (d) 1:4, and (e) 1:5 at 10000x magnifications.





**Figure 10:** SEM micrographs of PT film on PET deposited by the SILAR method. (a) one coating, (b) two coating, (c) three coating, (d) four coating, and (e) five coating at 10000x magnifications.

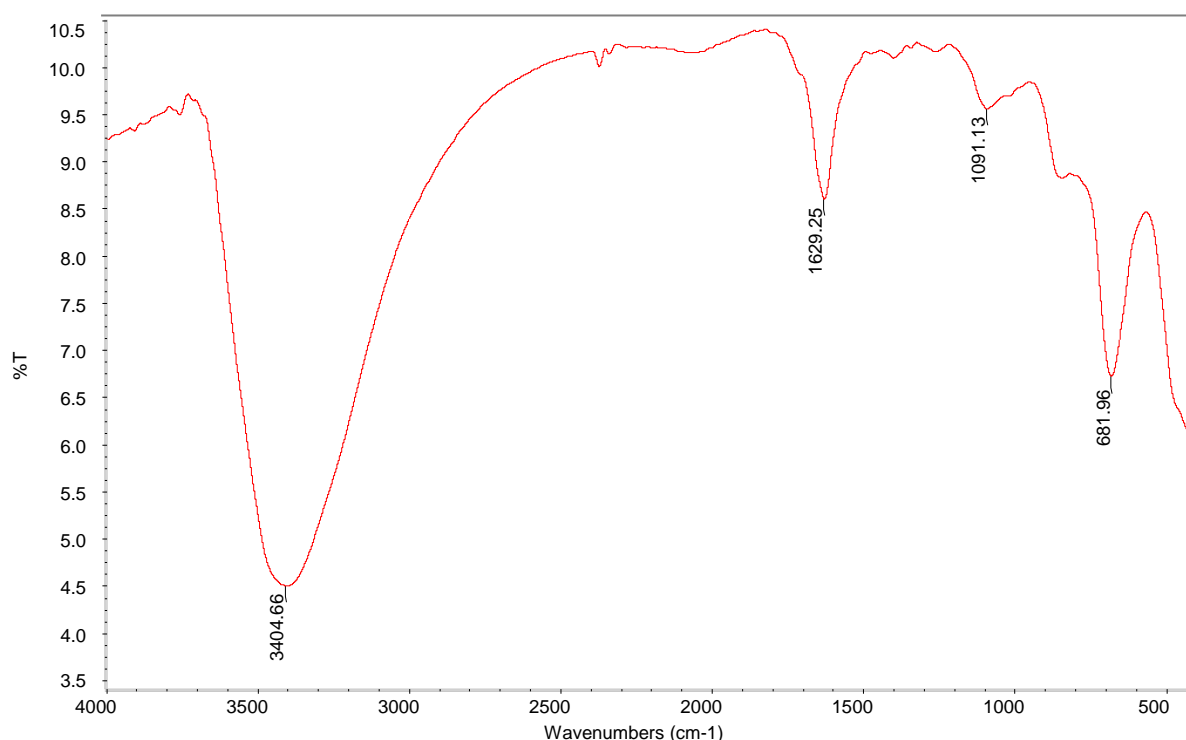
Figure 9 show the effect of oxidant concentration on the morphology of PT film deposited on PET. The surface morphology of KOH treated PET film showed substantially large and deep. In contrast, PT/PET film shows the presence of tiny coalesced grains randomly distributed over the substrate. Furthermore, as seen in SEM micrographs, the concentration of oxidant significantly affected the surface morphology of PT film deposited on the PET film. A smooth aggregate of PT layer which contained larger empty space was observed when monomer/oxidant molar ratio is 1:2 (Figure 9(b)). At the monomer/oxidant molar ratio of 1:3, smoother aggregates of PT layer which contained lesser empty spaces was observed (Figure 9(c)). This smoother and more uniform layer led to the highest conductivity of PT film deposited with a monomer/oxidant molar ratio of 1:3. At the monomer/oxidant of 1:4, the PT particles grew into denser aggregates and more coalesced grains present within the layer (Figure 9(d)). At the monomer/oxidant molar ratio of 1:5, the PT layer was observed to contain large coalesced grains with randomly distributed and crack line adhere on the PET substrate (Figure 9(e)). The observed crack phenomena might be due to the high yield of polythiophene coated on PET substrate and eventually leads to high internal stress which resulted in brittle cracks in the surface morphology (Wang *et al.* 2009).

Figure 10 shows the effect of relative thickness on the morphology of PT film deposited on PET substrate. Increasing the number of coating would lead to different surface morphology from less dense aggregates to denser surface and more coalesced grains. In Figure 10(a), relative smooth aggregates of PT layer with empty spaces were observed. With increasing number of coating, the number of coalesced grains increased, and became a relative smoother layer (Figure 10(b) to (c)). Moreover, the needle-like PT particles as observed in Figure 10(d) became denser, distributed more evenly, lastly the needle-like PT

particles tend to agglomerate (Figure 10(e)). Based on the conductivity measurement, the surface morphology of PT film shown in Figure 10(d), exhibited the highest conductivity.

#### 4.2.4 Fourier transforms infrared spectroscopy (FTIR)

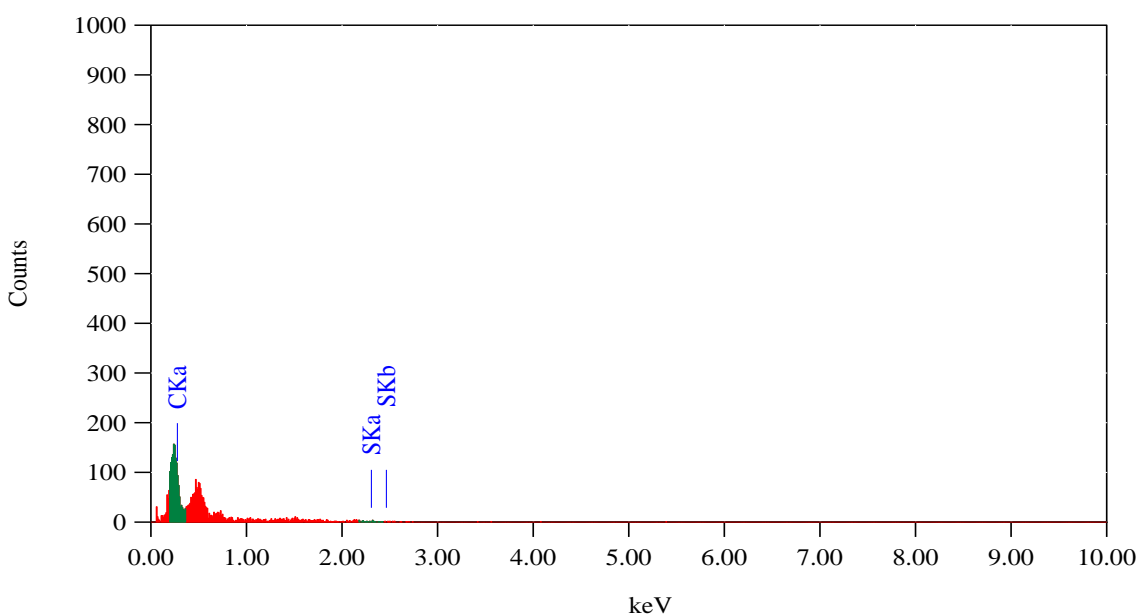
The FTIR spectrum of PT showed an absorption band at about  $3404\text{ cm}^{-1}$  which was associated with the O-H stretching of water in KBr (Nasrollahzadeh *et al.*, 2013). The absorption band at around  $1629\text{ cm}^{-1}$  was due to C=C asymmetric vibration modes of thiophene ring (Kamat *et al.*, 2012). The absorption band at  $1091\text{ cm}^{-1}$  was attributed to C-S bond in polythiophene (Acharya *et al.*, 2010). The absorption band at  $682\text{ cm}^{-1}$  represented the C-S-C planar deformation of the thiophene ring (Kamat *et al.*, 2010). The absorption bands characteristics as shown in Figure 13 confirmed the formation of polythiophene.



**Figure 11:** FTIR spectrum of polythiophene film.

#### 4.2.5 Energy Dispersive X-Ray Analysis (EDX)

Figure 12 show the EDX spectrum of PT/PET and Table 1 show the element composition of polythiophene on PET. The presence of the trace of elements (sulfur and carbon) shown the film adhere was polythiophene. Table 1 revealed that most abundant element in the polythiophene was carbon with a mass percentage of 94.01%, followed by a mass percentage of 3.59% of oxygen and finally mass percentage of 2.4% of sulfur. The carbon and sulphur was attributed to polythiophene. However, the presence of O might due to the PET substrate used for the analysis (Rassie *et al.*, 2011). Furthermore, the presence of O also might due to oxidation of the polythiophene by atmospheric air after polymerization (Olayo *et al.*, 2010).



**Figure 12:** EDX result of PT/PET elemental analysis

**Table 1:** Element composition table of PT/PET

Element	Mass%
C	94.01
O	3.59
S	2.40
Total	100

#### 4.2.6 Electrical Conductivity

**Table 2:** Effect of the oxidant (FeCl<sub>3</sub>) concentration on the resistivity of PT/PET films

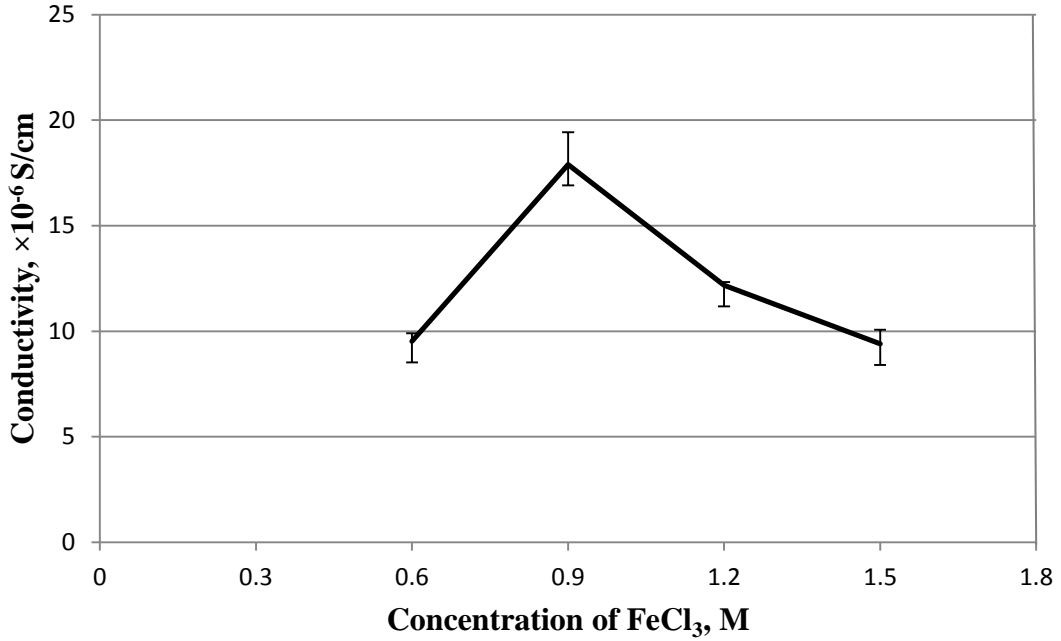
Concentration of FeCl <sub>3</sub> , (M)	Films resistivity, (kΩ.cm)
0.6	105.08
0.9	56.14
1.2	82.10
1.5	103.23

Table 2 shows the effect of the FeCl<sub>3</sub> concentration on the resistivity of PT/PET films. The resistivity of PT/PET films was measured using an ordinary digital multi-meter with a two point probe at a separation of 1.0 cm.

$$\text{Conductivity} = 1 / \text{Resistivity} \quad (1)$$

The resistivity of films is inversely proportional to conductivity (equation 1). This means that, the higher the resistivity, the lower the conductivity. As show in Table 2, the lowest resistivity (56.14 kΩ.cm) was achieved at 0.9 M of FeCl<sub>3</sub> whereas the highest resistivity (105.08 kΩ.cm) was achieved at 0.6 M of FeCl<sub>3</sub>. As shown in Figure 13, the conductivity is influenced by the concentration of oxidant. As concentration of the oxidant increase

(until 0.9 M), the conductivity increase from  $9.527 \times 10^{-6}$  S/cm to  $17.905 \times 10^{-6}$  S/cm respectively. This phenomena happens because, at higher concentration of  $\text{FeCl}_3$  will realize a higher doping level and longer  $\pi$ -conjugation length. In contrast, at very low concentration of  $\text{FeCl}_3$  will show low conductivity due to low probability of interaction between oxidant and monomer and thus not favourable the formation of PT with large  $\pi$ -conjugation (Mohammadizadeh *et al.*, 2014). Further increase of concentration above 0.9 M, the conductivity start to decrease to  $12.182 \times 10^{-6}$  S/cm and  $9.401 \times 10^{-6}$  S/cm at 1.2 M and 1.5 M of  $\text{FeCl}_3$  respectively. This is due to over-oxidation of PT chains (Huang *et al.*, 2009).

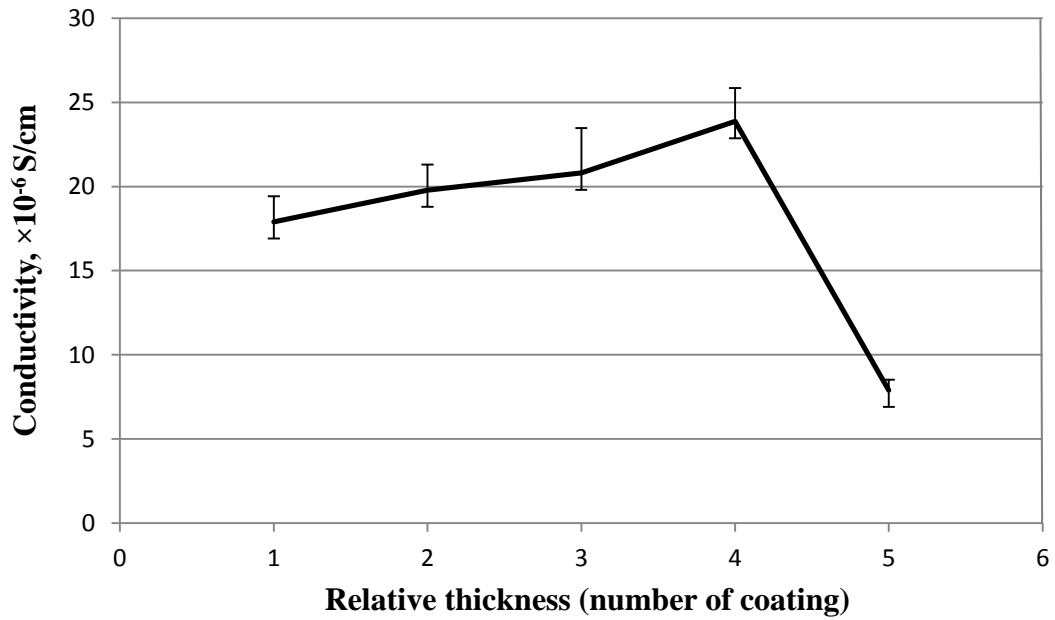


**Figure 13:** Effect of the oxidant ( $\text{FeCl}_3$ ) concentration on the conductivity of PT/PET films

**Table 3:** Effect of PT thickness on the resistivity of PT/PET films.

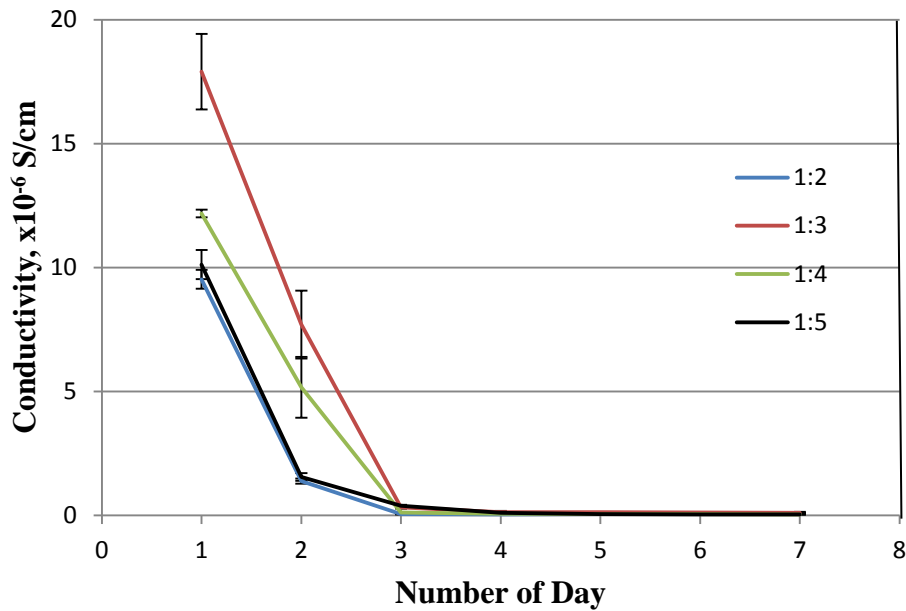
Relative thickness, (number of coating)	Films resistivity, (k $\Omega$ .cm)
1	56.140
2	50.735
3	48.569
4	42.078
5	127.027

The thickness of PT/PET is another factor which influences the resistivity of PT/PET films. As shown in Table 3, the films resistivity was observed to decrease as the number of PT coating was increased until four coating. However, high resistivity was observed with five coatings.



**Figure 14:** Effect of relative thickness on the conductivity of PT/PET films.

Figure 14 shows the effect of relative thickness of PT film on the conductivity of PT/PET based film. The conductivity, increase as relative thickness of PT film was increased with number of time of coating but was observed to decline with five coatings. From first time coating until fourth coating, the conductivity of PT/PET film increased from  $17.905 \times 10^{-6}$  S/cm to  $23.871 \times 10^{-6}$  S/cm respectively. The most optimum relative thickness for PT film to exhibit the highest conductivity was four coating and the conductivity as high as  $23.871 \times 10^{-6}$  S/cm. As the film thickness was increased, PT film was evenly distributed and denser on the PET film as compared to one layer of PT coating. Besides, five coatings of PT film on PET exhibited the lowest conductivity,  $7.905 \times 10^{-6}$  S/cm. Thick PT film would eventually act as an insulator and hence exhibited lower conductivity (Hasiah, *et al.*, 2008).



**Figure 15:** Aging time of electrical conductivity of polythiophene/polyethylene terephthalate in different monomer/oxidant ratio 1:2, 1:3, 1:4 and 1:5 respectively.

The aging time of electrical conductivity of PT/PET in different monomer/oxidant ratio was shown in Figure 15. As shown in Figure 15, the electrical conductivity decreased significantly among the different monomer/oxidant ratio from Day 1 to Day 3 and



become almost constant for Day 4 to Day 7. From day 1 to Day 2, the electrical conductivity in 1:2 monomer: oxidant ratio decreased 85.51%, 56.98% for 1:3 ratio, 57.58% for 1:4 ratio, and 84.66 for 1:5 ratio. Whereas, from Day 2 to Day 3, the electrical conductivity decrease significantly at 96.38%, 95.79%, 97.76% and 74.55% in 1:2, 1:3, 1:4: and 1:5 monomer/oxidant ratio respectively. The remaining day showed the electrical conductivity do not significantly decreased and almost became constant. In simply word, the electrical conductivity of polythiophene/polyethylene terephthalate decreased over seven day. The decreased of electrical conductivity phenomena might be due to the low environmental stability that caused by the remaining of reduction product,  $\text{FeCl}_2$  in the polythiophene film and lead to 'dedoping' of the polythiophene film (Denis, 1999).

## 5.0 Conclusion and Recommendation

In conclusion, conductive PT films of varying thickness have been deposited on polyethylene terephthalate. From this study, the optimum conditions to achieved highest conductivity are monomer/oxidant molar ratio of 1:3 and four times of coating respectively. However, the method used in this study was not desirable for the preparation of electrically conductive PET-based thin film due to difficulties of obtaining uniform polythiophene coating on PET film surface. Furthermore, the polythiophene layer did not adhered well onto the PET films.

There are few recommendations to further this study.

- Identify a suitable surfactant for the preparation of nano-sized polythiophene in the form of stable suspension.
- Identify suitable ways of functionalizing the PET film in order to enhance the adhesion of polythiophene onto PET film.
- Identify the alternative oxidant that can be incorporated well with the PET film in order to enhance the conductivity.
- Identify the best way/techniques for depositing polythiophene film onto PET substrate and retain the electrical conductivity as long as possible.

## 6.0 Reference

- Acharya, A., Mishra, R. and Roy, G. S. (2010) Characterization of CdSe/Polythiophene Nanocomposite by TGA/DTA, XRD, UV-vis Spectroscopy, SEM-EDX and FTIR. *Armenian Journal of Physics*, 3(3), pp. 1195-202.
- Acqua, L. D., Tonin, C., Varesano, A., Canetti, M., Porzio, W. and Catellani, M. (2008) Vapour Phase Polymerization of Pyrrole on Cellulose-Based Textile Substrates. *Synthetic Metals*, 15(5–6), pp. 379–386.
- Ali, M. K. M., Ibrahim, K., Hamad, O. S., Eisa, M. H., Faraj, M.G. and Azhari, F. (2010) Deposited Indium Tin Oxide (ITO) Thin Films by Dc-Magnetron Sputtering on Polyethylene Terephthalate Substrate (PET). *Romanian Journal of Physics*, 56(5-6), pp. 730-741.
- Amborski, L. E.& Flierl, D.W. (1953) Physical Properties of Terephthalate Polyethylene Films. *Industrial and Engineering Chemistry*, 45(10), pp. 2290-2295.
- Asadian, E., Shahrokhian, S., Zad, A. I. and Jokar, E. (2014) In-situ Electro-polymerization of Graphene Nanoribbon/polyanilinecomposite Film: Application to Sensitive Electrochemical Detection of Dobutamine. *Sensors and Actuators B: Chemical*, 196, pp. 582-588.
- Ates, M., Karazehir, T. and Sarac, A. S. (2012) Conducting Polymers and Their Applications. *Current Physical Chemistry*, 2, pp. 224-240.
- Can, M., Pekmez, K., Pekmez, N. and Yildiz, A. (1998) Electropolymerization of Thiophene With and Without Aniline in Acetonitrile. *Turkish Journal of Chemistry*, 22, pp. 47-53.
- Cheyilan, S., Morgera, A. F., Puigdollers, J., Voz, C., Setti, L., Alcubilla, R., Badenes, G., Bizzarri, P. C. and Lanzi, M. (2006) Study of a Thiophene-based Polymer for Optoelectronic Applications. *Thin Solid Films*, 497(1-2), pp. 16-19.
- Chiang, C. K., Fincher, C. R., Park, Jr. Y. W., Heeger, A. J., Shirakawa, H., Louis, E. J. Gau, S. C. & MacDiarmid, A. G. (1977). Electrical Conductivity in Doped Polyacetylene. *Physical Review Letters*, 39(17), 1098-1101.
- Chu, C. W., Wang, P. C., Liu, L. H., Mengistie, D. A., Li, K. H., Wen, B. J. and Liu, T. S.(2013) Transparent Electrodes Based on Conducting Polymers for Display Application. *Displays*, 34(4), pp. 301-314.
- Collins, G. E.and Buckley, L. J. (1996) Conductive Polymer-coated Fabrics for Chemical Sensing. *Synthetic Metal*, 78(2), pp. 93-101.
- Cowie, J. M. G. and Arrighi, V. (2007) *Polymers: Chemistry and Physics of Modern Materials (3<sup>rd</sup>)*. Boca Rota: CRC.
- Seyam, A. M., Oxenham, W. and Theyson, T. (2015) 17- Antistatic and Electrically Conductive Finishes for Textiles, in P Roshan (ed), *Functional Finishes for Textiles*, Elsevier, UK, pp. 513-553.

- Denis, F. C. and Ziegler, C. (1999) Structure and Properties of Oligothiophenes in the Solid State: Single Crystals and Thin Films, in F. C Denis (ed), *Handbook of Oligo- and Polythiophenes*, Wiley-VCH, New York, pp. 183-281.
- Donelli, I., Freddi, G. Nierstrasz, V. A. and Taddei, P.(2010) Surface Structure and Properties of Poly-(ethylene terephthalate)Hydrolyzed by Alkali and Cutinase. *Polymer Degradation and Stability*, 95(9), pp. 1542-1550.
- Erdogan, M. K., Karakisla, M. and Sacak, M. (2012) Preparation, Characterization and Electromagnetic Shielding Effectiveness of Conductive Polythiophene/Poly(ethyleneterephthalate) Composite Fibers. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, 49(6), pp. 473-482.
- Favaro, S. L., Rubira, A. F., Muniz, E. C. and Radovanovic, E. (2007) Surface Modification of HDPE, PP, and PET Films with  $\text{KMnO}_4/\text{HCl}$  Solution. *Polymer Degradation and Stability*, 92, pp. 1219-1226.
- Feng, X. Q. & Wang, X. S. (2002). Effects of Thickness on Mechanical Properties of Conducting Polythiophene Films. *Journal of Materials Science Letters*, 21, 715-717.
- Fichou, D. (Ed.). (1999) *Handbook of Oligo-and Polythiophenes*. New York: Wiley-VCH.
- Foroutani, K., Pourabbs, B., Sharif, M., Mohammadizadeh, M., Fallahian, M. and Khademi, S. (2014) Preparation of Conductive Flexible Films by In Situ Deposition of Polythiophene Nanoparticles on Polyethylene Naphthalate. *Materials Science in Semiconductor Processing*, 18, pp. 6-14.
- Gao, C. Y., He, T. and Liu, Y. X. (2005) Surface Modification of Poly(ethylene-terephthalate) via Hydrolysis and Layer-by-layer Assembly of Chitosan and Chondroitin Sulfate to Construct Cytocompatible Layer for Human Endothelial Cells. *Colloids and Surfaces B: Biointerfaces*, 46(2), pp. 117-126.
- Gnanakan, S. R. P., Rajasekhhar, M. and Subramania. A. (2009) Synthesis of Polythiophene Nanoparticles by Surfactant -assisted Dilute Polymerization Method for High Performance Redox Supercapacitors, *International Journal of Electrochemical Science*, 4(9), pp. 1289-1301.
- Gok, A., Omastova, M. and Yavuz, A. G. (2007) Synthesis and Characterization of Polythiophenes Prepared in the Presence of Surfactants, *Synthetic Metals*, 157(1), pp. 23-29.
- Hasiah, S., Ibrahim, K., Senin, H. B. and Halim, K. B. K. (2008) Electrical Conductivity of Chlorophyll with Polythiophene Thin Film on Indium Tin Oxide as P-N Heterojunction Solar Cell. *Journal of Physical Science*, 19(2), pp. 77-92.
- Huang, M. R., Li, X. G. and Li, J. (2009) Facile Optimal Synthesis of Inherently Electroconductive Polythiophene Nanoparticles. *Chemistry: A European Journal*, 15, pp. 6446- 6455.
- Inoue, M., Vazquez, C. C. and Inoue, M. B. (1999) Characterization of New Copper Sulphide Materials. *Superficies y Vacio*, 9, pp. 219-221.

- Jeon, S. S., Yang, S. J., Lee, K. J. and Im, S. S. (2010) A Facile and Rapid Synthesis of Unsubstituted Polythiophene with High Electrical Conductivity Using Binary Organic Solvents. *Polymer*, 51(18), pp.4069-4076.
- Kamat, S. V., Puri, V. and Puri, R. K. (2012) Room Temperature Synthesis and Characterization of Polythiophene Chemical Bath Deposition (CBD) Method. *Materials Chemistry and Physics*, 132(1), pp. 228-232.
- Kamat, S. V., Tamboli, S. H., Puri, V., Puri, R. K., Yadav, J. B. and Joo, O. S. Q (2010) Post deposition heating effects on the properties of polythiophene thin films. *Archives of Physics Research*, 1(4), pp.119-125.
- Kattimani, J., Sankarappa, T., Praveenkumar, K., Ashwajeet, J. S., Ramanna, R. Chandraprabha, G. B & Sujatha, T. (2014). Structure and Temperature Dependence of Electrical Conductivity in Polythiophene Nanoparticles, *International Journal of Advanced Research in Physical Science*, 1(7), 17-21.
- Kaynak, A. and Beltrann, R. (2003) Effect of Synthesis Parameters on the Electrical Conductivity of Polypyrrole-coated Poly(ethyleneterephthalate) Fabrics. *Polymer international*, 52(6), pp. 1021-1026.
- Kelkar, D. & Chourasia, A. (2011). Structural Properties of Polythiophene Doped with FeCl<sub>3</sub>. *Chemistry & Chemical Technology*, 5(3), 309-315.
- Kim, Y. H., Sachse, C., Machala, M. L., May, C., Meskamp, L. M. and Leo, K. (2011) Highly Conductive PEDOT: PSS Electrode with Optimized Solvent and Thermal Post-treatment for ITO-free Organic Solar Cells. *Advanced Functional Materials*, 21(6), pp. 1076–1081.
- Konagaya, S., Abe, K. and Ishihara, H. (2002) Conductive Polymer Composite PET Film with Excellent Antistatic Properties. *Plastics, Rubber and Composites: Macromolecular Engineering*, 31(5), pp. 201-204.
- Kuhn, H. H. (1997) Adsorption at the Liquid/solid Interface: Conductive Textiles used on Polypyrrole. *Textile Chemist and Colorist*, 29(12), pp. 17-21.
- Kumar, D. and Sharma, R. C. (1998) Review Article: Advances in Conductive Polymers. *European Polymer Journal*, 34(8), pp. 1053-1060.
- Lange, U. and Mirsky, V. M. (2011) Integrated Electrochemical Transistor as a Fast Recoverable Gas Sensor. *Analytica Chimica Acta*, 687(1), pp. 7-11.
- Lechat, C. Bunsell, A. R., Davies, P. and Piant, A. (2006) Mechanical Behaviour of Polyethylene Terephthalate & Polyethylen Naphthalate Fibres Under Cyclic Loading. *Journal of Materials Science*, 41(6), pp. 1745-1756.
- Li, X. G., Li, J. and Huang, M. R. (2009) Interfacial Synthesis and Widely Controllable Conductivity of Polythiophene Microparticles. *The Journal of Physical Chemistry B*, 113(29), pp. 9718-9727.

- Liu, R. C. and Liu, Z. P. (2009) Polythiophene: Synthesis in Aqueous Medium and Controllable Morphology. *Chinese Science Bulletin*, 54(12), pp. 2028-2032.
- Macasaquit, A. C., and Binag, C. A. (2010) Preparation of Conducting Polyester Textile by in Situ Polymerization of Pyrrole. *Philippine Journal of Science*, 139(2), pp.189-196.
- Macdonald, W. A. (2004) Engineered Films for Display Technologies. *Journal of Materials Chemistry*, 14, pp. 4-10.
- Mohammadizadeh, M, Pourabbas, B., Mahmoodian, M., Foroutani, K. and Fallahian, M. (2014) Facile and Rapid Production of Conductive Flexible Films by Deposition of Polythiophene Nanoparticles on Transparent Poly(ethyleneterephthalate): Electrical and Morphological Properties. *Material Science in Semiconductor Processing*, 20, pp. 74-83.
- Mohammadizadeh, M., Pourabbas, B., Foroutani, K. and Fallahian, M. (2015) Conductive Polythiophene Nanoparticles Deposition on Transparent PET Substrates: Effect of Modification with Hybrid Organic-inorganic Coating. *IJE Transactions A: Basic*, 28(4), pp. 567-572.
- Nalwa, H. S. (Ed.). (2001). *Handbook of Advanced Electronic and Photonic Materials and Devices*. London: Academic Press.
- Nasrollahzadeh, M., Jahanshahi, M., Salehi, M., Behzad, M. and Narollahzadeh, H. (2013) Synthesis and Characterization of Nanostructured Polythiophene in Aqueous Medium by Soft-template Method. *Journal of Applied Chemistry*, 8(27), pp. 31-34.
- Olayo, M. G., Cruz, G. J., Lopez, S., Morales, J. and Olayo, R. (2010) Conductivity and Activation Energy in Polymers Synthesized by Plasmas of Thiophene. *Journal of the Mexican Chemical Society*, 54(1), pp.18-23.
- Onoda, M., Abe, Y. and Tada, K. (2009) New Fabrication Technique of Conductive Polymer/insulating Polymer Composite Films and Evaluation of Biocompatibility in Neuron Cultures. *Thin Solid Films*, 518, pp. 743-749.
- Patil, B. H., Jagadale, A. D., & Lokhande, C. D. (2012) Synthesis of polythiophene thin films by simple successive ionic layer adsorption and reaction (SILAR) method for supercapacitor application. *Synthetic Metals*, 162, pp. 1400-1405.
- Pecher, J. and Mecking, S. (2010) Nanoparticles of Conjugated Polymers. *Chemical Reviews*, 110(10), pp. 6260-6279.
- Ramakrishnan, S. (2011) Conducting Polymers: From a Laboratory Curiosity to the Market Place. *Resonance*, 2(11), pp. 48-58.
- Rassie, C., Olowu, R. A., Waryo, T. T., Wilson, L., Williams, A., Baker, P. G. and Iwuoha, E. I. (2011) Dendritic 7T-Polythiophene Electro-Catalytic Sensor System for the Determination of Polycyclic Aromatic Hydrocarbons. *International Journal of Electrochemical Science*, 6, pp. 1949-1967.

- Reddish, W. (1950) The Dielectric Properties of Polyethylene Terephthalate (Terylene). *Transaction of the Faraday Society*, 46, pp. 459-475.
- Reyman, D., Guereca, E. and Herrasti, P. (2007) Electrodeposition of Polythiophene Assisted by Sonochemistry and Incorporation of Fluorophores in the Polymeric Matrix. *Ultrasonics Sonochemistry*, 14, pp. 653-660.
- Ryu, H. W., Kim, Y. S., Kim, J. H. and Cheong, I. W. (2014) Direct synthetic route for water-dispersible polythiophene nanoparticles via surfactant-free oxidative polymerization. *Polymer*, 55, pp. 806-812.
- Senthilkumar, B., Thenamirtham, P. and Selvan, R. K. (2011) Structural and Electrochemical Properties of Polythiophene. *Applied Surface Science*, 257(21), pp. 9063-9067.
- Seyam, A. M., Oxenham, W. and Theyson, T. (2015) 17- Antistatic and Electrically Conductive Finishes for Textiles, in P Roshan (ed), *Functional Finishes for Textiles*, Elsevier, UK, pp. 513-553.
- Tallman, D. E. Spinks, G., Dominis, A. and Wallace, G. G. (2002) Electroactive Conducting Polymers for Corrosion Control. *Solid State Electrochem*, 6(2), pp. 73-84.
- Tho, S. Y. and Ibrahim, K. (2012) Influence of Surface Roughness of Polyethylene Terephthalate (PET) Substrate to the Morphology and Optical Properties of Coated Zinc Oxide Thin-film. *Jurnal Teknologi*, 59, pp. 5-8.
- Varesano, A. Acqua, L. D. and Tonin, C. (2005) A Study on the Electrical Conductivity Decay of Polypyrrole Coated Wool Textiles. *Polymer Degradation and Stability*, 89(1), pp. 125-132.
- Venkatachalam, S., Nayak, S. G., Labde, J. V., Gharal, P. R., Rao, K. and Kelkar, A. K. (2012) Degradation and Recyclability of Poly (Ethylene Terephthalate). *Material Science in Semiconductor Processing*, 20, pp. 89-101.
- Wadatkhar, N. S. and Waghuley, S. A. (2012) Study of Chemically Synthesized Polythiophene. *International Journal of Basic and Applied Research Special Issue*, 51(2), pp. 51-53.
- Wang, X. S., Tang, H. P., Li, X. D. and Hua, X. (2009) Investigations on the Mechanical Properties of Conducting Polymer Coating –Substrate Structure and Their Influencing Factors. *International Journal of Molecular Sciences*, 10, pp. 5257-5284.
- Wang, L., Wang, X. and Lin, T. (2010) 6-Conductive coatings for textiles. In: SMITH, W. C. (ed.) *Smart textile coatings and laminates*. Cambridge: Elsevier, pp. 155-188.
- Wen, L., Jeong, d. C., Javid, M., Kim, S., Nam, J. D., Song, C. and Han, J. G. (2014) Conductive Polythiophene-like Thin Film Synthesized Using Controlled Plasma Processes, *Thin Solid Films* [Online]. Available at: <http://www.sciencedirect.com/science/article/pii/S0040609014012899> [Accessed: 5 May 2015].

- Wiener, J. Ramadan, M. A., Gomaa, R., Abbassi, R. and Hebeish, A. (2013) Preparation and Characterization of Conductive Cellulosic Fabric by Polymerization of Pyrrole. *Materials Sciences and Application*, 4(10), pp. 649-655.
- Youssef, A. M., Samahy, M. A. E. and Rehim, M. H. A. (2012) Preparation of Conductive Paper Composites Based on Natural Cellulosic Fibers for Packaging Application. *Carbohydrate Polymers*, 89(4), pp. 1027-1032.
- Zhang, H. Q., Hu, L. W., Tu, J. G. and Jiao, S. Q. (2014) Electrochemically Assembling of Polythiophene Film in Ionic Liquids (ILs) Microemulsions and its Application in an Electrochemical Capacitor. *Electrochimica Acta*, 120, pp. 122-127.



## Appendix

**Appendix A:** Effect of the oxidant ( $\text{FeCl}_3$ ) concentration on the resistivity (with the three replicate raw data) of PT/PET films

Concentration of oxidant, $\text{FeCl}_3$	Films resistivity, $\text{k}\Omega\cdot\text{cm}$			
	Replicate 1	Replicate 2	Replicate 3	Mean
0.6	109.58	104.54	101.12	105.08
0.9	52.928	61.92	53.56	56.14
1.2	83.26	81.72	81.32	82.10
1.5	101.244	92.7	115.76	103.23

**Appendix B:** Effect of relative thickness on conductivity (with the three replicate raw data) of PT/PET films.

Relative thickness, number of coating	Films resistivity, $\text{k}\Omega\cdot\text{cm}$			
	Replicate 1	Replicate 2	Replicate 3	Mean
1	52.928	61.92	53.56	56.14
2	51.16	46.706	54.34	50.735
3	41.952	50.59	53.164	48.569
4	42.916	44.96	38.358	42.078
5	116.48	135.86	128.74	127.027

**Appendix C:** The electrical conductivity of different monomer/oxidant molar ratio, 1:2, 1:3, 1:4, and 1:5 respectively within the seven day

<b>Day</b>	<b>Conductivity x10<sup>-6</sup> S/cm</b>			
	<b>1:2</b>	<b>1:3</b>	<b>1:4</b>	<b>1:5</b>
<b>1</b>	9.5270	17.9050	12.1817	10.1170
<b>2</b>	1.3803	7.7027	5.1683	1.5517
<b>3</b>	0.0498	0.3240	0.1163	0.3947
<b>4</b>	0.0393	0.1347	0.0708	0.1013
<b>5</b>	0.0537	0.1343	0.0540	0.0497
<b>6</b>	0.0721	0.1183	0.0518	0.0440
<b>7</b>	0.0494	0.1101	0.0471	0.0417